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Evaluation of Stationary Source Particulate Measurement Methods Volume II. Oil-Fired Steam Generators

Arthur D. Little, Inc, Cambridge, Mass

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16. ABSTRACT

An experimental study was conducted to determine the reliability of the Method 5 procedure for providing particulate emission data from an oil-fired steam generator. The study was concerned with determining whether any "false" particulate resulted from the collection process of from the collected particulate. Variations to Method 5 tested included filter media, size and temperature, nozzle type and sampling duration. Tests were conducted at a 350 MW source utilizing low sulfur residual fuel.

Two series of field tests were conducted. In both cases simultaneous samples were collected with two trains. In all cases one train was the standard Method 5 train. The other train was either a modified Method 5 train with an in-stack filter or a second standard Method 5 train.

Runs were preformed in which one or both trains were spiked with SO_2 at the nozzle to provide sampled gas stream concentrations of ~2000 ppm SO_2 approximating a high sulfur fuel. By comparing particulate and sulfate distributions between probe and filter catches for the two trains, no evidence for the formation of "false particulate" for the condition evaluated were found.

The in-stack filter method used has several advantages over EPA Method 5 including the elimination of recovering the probe catch.

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EVALUATION OF STATIONARY SOURCE PARTICULATE MEASUREMENT METHODS

Volume II Oil-Fired Steam Generators

by

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ABSTRACT

An experimental study was conducted to determine the reliability of the Method 5 procedure for providing particulate emission data from an oil-fired steam generator. The study was concerned with determining first, whether any "false" particulate, e.g., particulate formed as a result of the collection process, was associated with Method 5 sampling and second, the influence on collected particulate, if any, associated with parametric variations to Method 5, including filter media, size and temperature, nozzle type and sampling duration. Tests were conducted at a 350 MW source utilizing low sulfur residual fuel. Stack gases contained approximately 200 ppm SO_2 and 1-2 ppm SO_3. A first series of field tests included simultaneous sample collection with two trains, one a Method 5 train and the other modified to incorporate a flat in-stack filter; the latter was employed as a control with the former being varied with respect to filter media (glass fiber versus quartz), filter temperature (120°C versus 160°C) and sampling duration (1 versus 2 hrs). Additional runs were performed in which one or both trains were spiked with SO_2 at the nozzle to provide sampled gas stream concentrations of ~2000 ppm SO_2 as an approximation of the combustion gases from a high sulfur fuel. By comparing particulate and sulfate distributions between probe and filter catches for the two trains, it was determined that there was no evidence for the formation of "false particulate" for the conditions evaluated. Furthermore, it was found that the in-stack train particulate catch (nozzle and filter) was approximately 20 percent higher than for the Method 5 train; the data for Method 5 train indicated the need for a blank correction of ~10 mg/m^3. These observations are believed to be the result of an inability to make a quantitative recovery of the probe catch. A second set of twelve statistically designed, paired experiments was carried out with Method 5 trains varied with respect to filter size and temperature and nozzle type. An analysis of variance performed on the data indicated that the nozzle type and filter temperature-size interaction can have a statistically significant result, corresponding to a variance in result of 7 mg/m^3 out of a total average catch of 31 mg/m^3. Most of the standard error in the measurement, corresponding to 5 mg/m^3, is associated with the probe catch. Based upon these results, particulate sampling with an in-stack collector appears to have an advantage over Method 5 sampling, in that the need for recovering the probe catch is eliminated. Furthermore, for stack gas streams having SO_2 concentrations higher than 2 ppm, no increase to the particulate level (for the in-stack train) due to condensation of SO_3 along the probe or on the external filter should result, such as would occur in the Method 5 train if these components were maintained at 120°C. Finally, an in-stack train could be much simpler in terms of design, operation and sample recovery as compared to the Method 5 procedure.

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1. INTRODUCTION

In response to the provisions of the Clean Air Act of 1970, the EPA has identified stationary source categories that contribute significantly to air pollution. Standards of performance applicable to new sources within the listed categories have been promulgated for twelve source categories and have been proposed for an additional twelve. These regulations provide emission limits for various pollutant species and specify the test methods that are to be utilized in determining compliance with the performance standards.

Of the various source categories presently identified as contributing to air pollution, fifteen are regulated with respect to particulate emissions. Particulate is identified as "any material, other than uncombined water, which exists in a finely divided form as a liquid or solid at standard conditions (20°C, 760 mm Hg)," and is measured by EPA Method 5, "Determination of Particulate Emissions from Stationary Sources." A listing of regulated industries, maximum permissible particulate emission levels and appropriate test methods is given in Table 1.

During the three years since promulgation of the Method 5 test procedure, a variety of comments has been made regarding its reliability and its usability in measuring the particulate burden within source emissions. The following types of questions are typical.

- Does Method 5 yield accurate values for the particulate emission levels of the effected sources?
- Are there chemical interactions involving transformation from gas phase to particulate taking place in the probe, on the filter or anywhere else in the system that might influence the particulate concentration?
- Does the moisture content, temperature or chemical composition of the gases present influence the results or sampling procedure in any way?
- Are the chemical compounds and/or elements present in the collected particulates characteristic of this type of source? If characteristic, to what degree; if not, have they been changed in any way by the collection process?
- Do selected variations in the Method 5 testing procedure have an influence on results?
- Do alternative sampling techniques or train components provide more reliable emission values?
- Are there special sampling problems that are specific to just one or to a few source categories?

TABLE 1

STATIONARY SOURCE PARTICULATE EMISSION STANDARDS

Reference	Subpart	Source	Standard for Particulate Matter
	Promulgated		
1	D	Fossil Fuel-Fired Steam	180 mg/10^6 cal
1	E	Incinerator	180 mg/m^3
1	F	Portland Cement	136 g/ton of feed
2	I	Asphalt Concrete	90 mg/m^3
2	J	Petroleum Refinery	1 kg/1000 kg coke burnoff
2	L	Secondary Lead	50 mg/m^3
2	M	Secondary Brass & Bronze	50 mg/m^3
2	N	Iron and Steel (BOF)	50 mg/m^3
2	O	Sewage Treatment	65 g/kg dry sludge
	Proposed		
3	P	Primary Copper	50 mg/m^3
3	Q	Primary Zinc	50 mg/m^3
3	R	Primary Brass	50 mg/m^3
4	Y	Coal Preparation	40 mg/m^3
5	Z	Ferroalloy Production	230 or 460 g/mw-hr.
6	AA	Steel (Electric Arc)	12 mg/m^3
	Methods		
1	1	Sample and velocity traverses for stationary sources	
1	2	Determination of stack gas velocity and volumetric flow rate (Type S pilot tube)	
1	3	Gas analysis for carbon dioxide, excess air and dry molecular weight	
1	5	Determination of particulate emissions	

References

1 Federal Register 36 24875-24895 (December 23, 1971); 39 20790-20794 (June 14, 1974)
2 Federal Register 39 9307-9323 (March 8, 1974); 13278 (April 17, 1974)
3 Federal Register 39 37039-37049 (October 16, 1974)
4 Federal Register 39 37922-37924 (October 24, 1974)
5 Federal Register 39 37466-37468, 37470-37472 (October 21, 1974)

- To what degree do process variables influence sampling procedures or results?

To address these areas of concern, the EPA is sponsoring several research investigations, each directed toward a specific stationary source category. The present report relates to oil-fired steam generators. A study of coal-fired boilers has also been conducted by Arthur D. Little, Inc., and is reported separately. Other investigators have considered incinerators, Portland cement plants, asphalt concrete plants and BOF steelmaking.

With respect to fossil-fuel steam generation, generally utilizing fuels with a sulfur content of 0.5 to 3.0%, the sampling and analysis methods developed to date have not adequately considered the chemical and physical changes that can occur during the collection process which may lead to the formation of what is expressed empirically as "false particulate". Thus, the present Method 5 procedure may not accurately reflect the particulate burden to the atmosphere as it would exist in a dispersed plume.

False particulate, i.e., the matter that would not have formed in the atmosphere at 20°C and 760 mm Hg, represents the increase in collected mass due to the collection process itself. For example, particulate that is collected near the start of a test, distributed along the probe walls and on the filter, is continually exposed to the freshly sampled stream; there is thus an opportunity for catalytic oxidation of SO_2 to SO_3, physi- and chemisorption of organic vapors on particulate, hydration of compounds or compound conversion. In practice, all may occur to some degree. The result is that various stationary source industries could be found to be out of compliance due to appreciable but inappropriate levels of "false particulate."

The current program has investigated the influence of selected variations in sampling procedure and train configuration upon particulate levels. In almost all cases, simultaneous sampling with two trains was carried out to permit a direct comparison of results. Samples were analyzed to identify any sampling conditions leading to false particulate as well as to determine the difference in result for various collection procedures.

Sampling was conducted at a single point rather than by point-to-point traverses. Thus, the comparative values of loading per unit volume of gas reported herein do not represent emission values as would be determined by a compliance test. They do, however, indicate the general range that would be found by compliance testing.

II. PROGRAM PLAN FOR OIL-FIRED BOILER EMISSIONS

A. Experimental Considerations

This program was conducted to develop the background and understanding necessary to evaluate the accuracy and reliability of EPA Method 5 for measuring particulate emissions from oil-fired steam generation plants. The scope of work included the following elements:

Investigate the possibility of "false particulate" formation within a Method 5 train.

Determine if minor modifications to the Method 5 train or sampling procedure influences the amount or nature of the particulate catch.

Evaluate alternate particulate collection procedures which may have advantage over Method 5 in terms of accuracy, simplicity of apparatus or procedure, etc.

To investigate experimentally these areas, two independent sets of tests were conducted at an oil-fired electric utility. The design of individual experiments was formulated on the basis of source and sampling variables considered to have an influence on emission measurements. Parameters that were considered included:

Source

Particulate - loading, chemical characteristics, particle size distribution
SO_2, SO_3 concentration
Stack temperature
Uniformity of conditions as a function of time

Sampling

Sampling train design
Filter size
Filter media
Nozzle configuration
Sampling time
System temperature
Sampling rate

Beyond the selection of a feasible location, little can be done regarding source parameters. Once a site is chosen, experimental plans must be developed around typically existing conditions. Sampling parameters, on the other hand, are readily adjusted and can influence the amount and distribution (within the sampling train) of the collected particulate. Sampling time depends largely upon particulate loading levels within the sampled stream, but should not be so short as to be influenced by process fluctuations; the range of 30 to 120 minutes is probably most suitable.

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Collection rate can be important in terms of the opportunity for stream components to interact with particulate that has already been collected. The chemical reactivity between the gas stream and sampling train materials represents an important category of sampling variables. This includes filter media (silica, borosilicate glass, etc.) probe liner (glass, stainless), etc. Filter size can presumably influence the collection efficiency of particulate as it reflects the face velocity of the approaching gas stream. Nozzle configuration (90° or button hook) is considered as it may influence the distribution of particulate within the system. Finally, the temperature profile within the system may have a major influence upon the preferential condensation of vapor or rates of reaction between species of the sampled stream.

Previously mentioned factors were taken into account during preparation of the sampling plan, and consultation with EPA personnel and the other contractors resulted in mutually agreed upon sets of experiments. To facilitate evaluation of these variables, simultaneous sampling was conducted with two sampling trains as described in the next section.

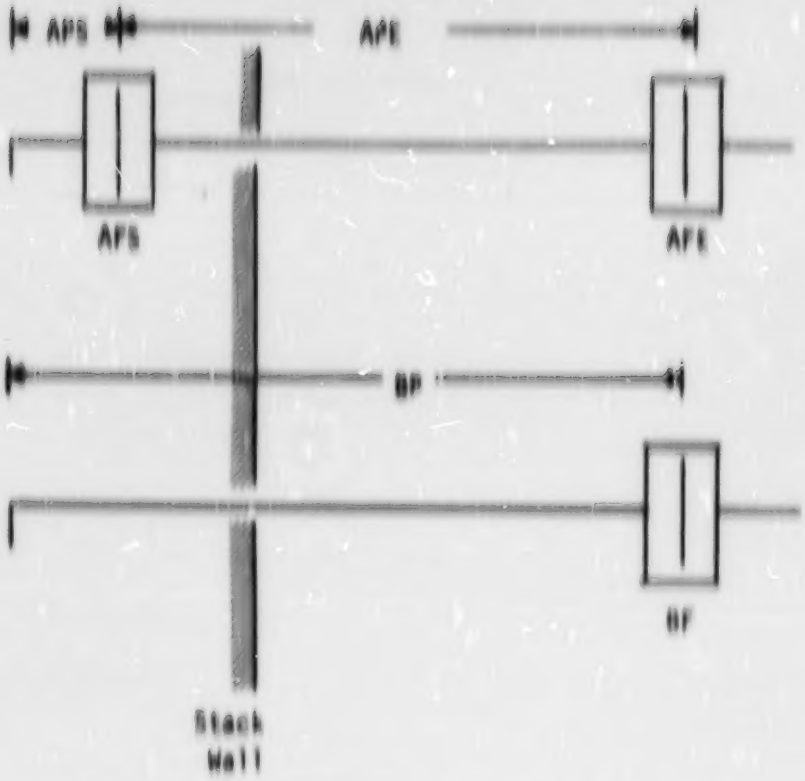
B. Sampling Apparatus

Two Method 5 particulate sampling trains were employed during this study. Both were modified versions of the Research Appliance Company "Stak-sampler." The configuration of the sampling systems were varied to accommodate the purpose of the various experiments. A schematic sketch of the two trains is presented in Figure 1.

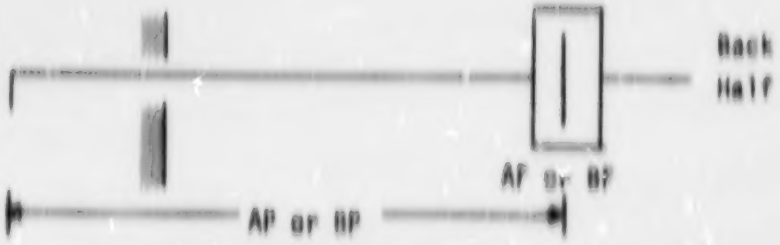
For the first set of experiments investigating "false particulate" formation, one sampling train was modified by the inclusion of a stainless steel filter holder between the nozzle and probe assemblies. Both trains included an external filter and a series of four impingers charged as outlined in the Federal Register.* Samples collected from the various train components were given the following codes:

AFS	Instack filter, A train
AFE	External filter, A train
APS	Washings from nozzle and front half of instack filter holder, A train
APE	Washings from back half of instack filter holder, probe and front half of external filter holder, A train
BF	External filter, B train
BP	Washings from nozzle, probe and front half of the external filter holder, B train

*Federal Register, 36, 15704-15722 (August 17, 1971).



A. FORMATION OF "FALSE PARTICULATE" EXPERIMENTS



B. REPRODUCIBILITY EXPERIMENTS

FIGURE 1 SCHEMATIC SKETCH OF PARTICULATE SAMPLING TRAINS

The train configurations utilized during the second phase of this study, during which the reproducibility of results as a function of train configuration was investigated, were basic Method 5 arrangements. For these tests, the nozzle design (90° versus button hook) and external filter size (6.3 versus 10.0 cm) were varied according to a statistically designed grid of experiments. Samples collected under this scheme were coded as follows:

AP	Washings of probe, nozzle and front half of external filter holder, A train
AF	External filter, A train
BP	Washings of probe, nozzle and front half of external filter holder, B train
BF	External filter, B train

Additional equipment utilized during the evaluation included a SO2/SO3 sampling train, designed and constructed by ADL, as well as velocity probes, an Orsat gas analyzer and proportional temperature controllers.

C. Source Description

Sampling was conducted at a New England power station equipped with two oil-fired 350 MW boilers. The facility utilizes a low sulfur residual oil with a magnesium oxide additive as a corrosion inhibitor. All sampling was performed on Unit No. 2 which typically develops a load of 360 MW on a fuel flow of 180,000 pounds per hour. Combustion is carried out with about 30% excess air, employing 1 gallon of scale preventive per 3000 gallons of fuel. Sampling was conducted in the stack upriser during after roughly 30 feet of straight run. A sketch of this duct is given in Figure 2. Typical stack conditions are as follows:

Stack temperature	145 - 155°C
Velocity	24 - 26 m/sec
Stack Pressure	4.7 - 5.0 mm Hg
Duct Dimensions	3.66 m diameter
Stack Gas Volume	260 - 270 m^3/sec
Port Size	10.2 cm nipple
Moisture	9 - 11%
O_2	3.5 - 5.0%
CO_2	9 - 12%
SO_2	200 - 250 ppm
SO_3	1 - 3 ppm

Field work was performed in two stages; the first set of experiments was conducted during April-May 1973 and the second set during June-July 1974.

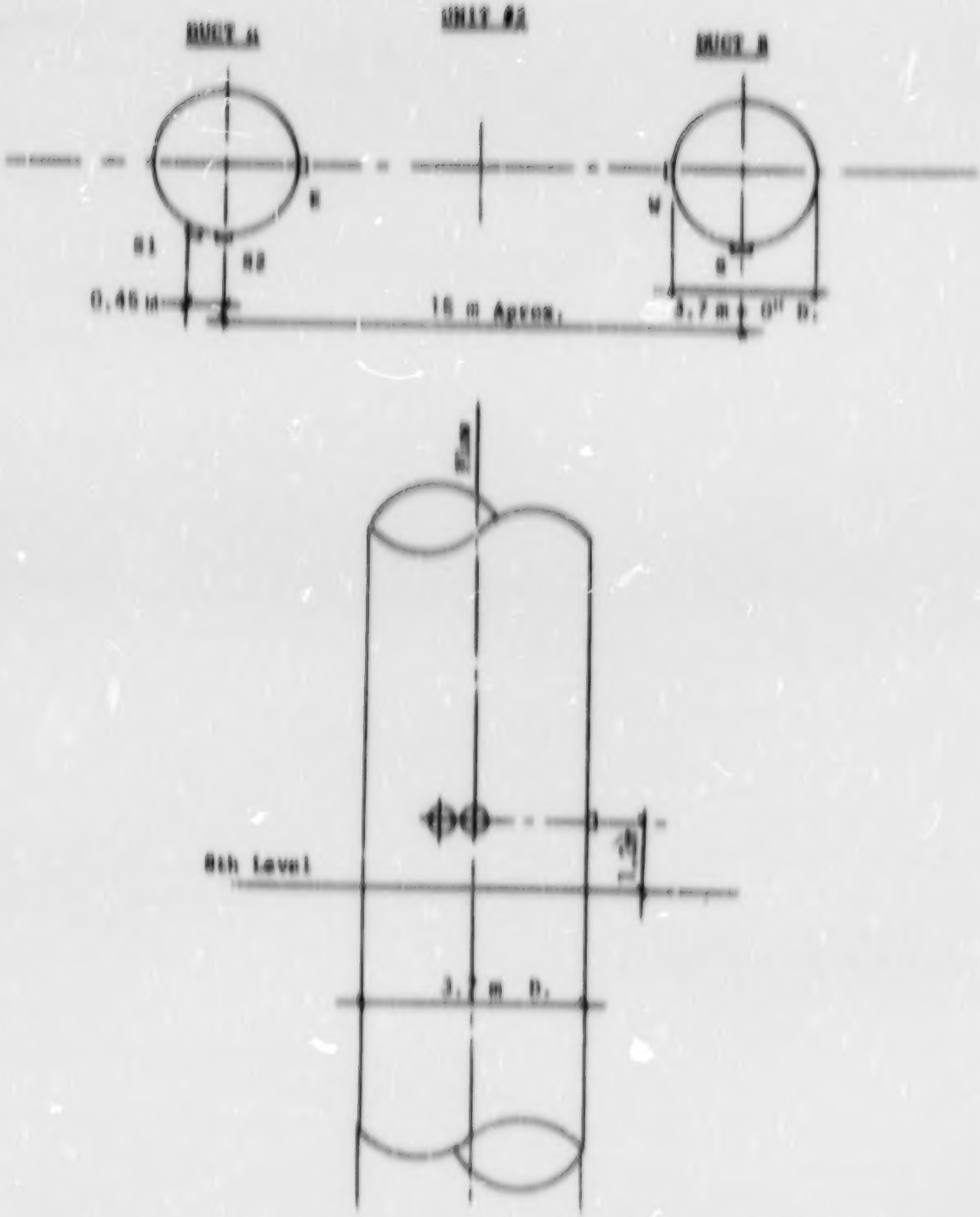


FIGURE 2 SKETCH OF SAMPLING PORT LOCATIONS FOR OIL-FIRED BOILER

III. EXPERIMENTAL PROCEDURE

A. Sampling Plan

To permit a comparison of results from several stationary sources, the various contractors collaborated as much as possible with respect to the design of experimental tests and commonality of equipment and sampling procedures. Based upon discussions of our test plan with the EPA Project Officer, the task of evaluating oil-fired boilers was separated into two experimental sets of tests. These were designed to provide information relevant to the formation of false particulate and to a parametric study of Method 5, respectively.

1. Formation of False Particulate

To evaluate the possibility of false particulate formation, a series of twelve experiments were proposed in which the research-type A train was run as the control and the Method 5 B train was varied according to the following experimental block.

		L_1	L_2
F_1	T_1	X	X
	T_2	X	X
F_2	T_1	X X	X X
	T_2	X X	X X

where

X = sample to be obtained
T = temperature of external filter, B train (T_1 = 120°C; T_2 = stack temperature or 175°C, whichever is lower)
F = filter media, B train (F_1 = MSA 1106 BH glass fiber; F_2 = Modified Quartz Fiber* - MQF)
L = level of loading (L_1 = reasonable sample catch, i.e., 100 mg; L_2 twice sampling time of L_1)

*Pallflex "Tissuequartz" subjected to a strengthening treatment developed by ADL under EPA Contract No. 68-02-0585.

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As indicated by the grid, three variables (effects) were selected as having a possible influence on the formation of false particulate, with two conditions (levels) of each being evaluated. Data for the MM5 filter type was replicated to permit an evaluation of reproducibility.

The research-type A train was proposed to be the control, being equipped with an instack filter to capture all particulate as it exists within the stack, an external filter temperature maintained at 120°C and MM5 filter media for both the instack and external filter. The A train data was intended to give an indication of the source variability.

The experiment design called for simultaneous sampling with both A and B trains. Evaluation of the performance of the two trains was to be carried out by comparing the levels and distributions of particulate mass and sulfate content.

In addition to the twelve duplicate runs proposed in the grid, several other experimental runs were proposed to study specifically the possibility for SO_2 oxidation. These additional experiments and their purpose were as follows:

1. Spike both trains with an order of magnitude enrichment in SO_2. Is there an increase in $SO_4^=$ associated with any component of the sampling train?

2. Run both trains as Method 5 trains.

   a. Perform consecutive runs without cleaning probe in between. Does a dirty probe show differences from a clean one relative to sulfate/particulate ratio?

   b. Spike one train with an order of magnitude enrichment in SO_2. Are comparable results obtained between the two trains?

   c. Use a soiled filter (containing a measured particulate loading) from a prior run as a backup to a clean filter in one of the trains.
      Is there additional weight pickup signifying SO_2 reaction with the filter catch?
      Does the unsoiled backup filter exhibit a gain in weight, implying an influence from the filter media?

To permit selective spiking of the sampled gas with SO_2, a 1/8 inch diameter length of stainless steel tubing was tapped into the midsection of the nozzle and silver soldered in place. The other end of the tubing was connected through a rotometer to a tank of SO_2. During sampling, proportionate amounts of SO_2 were bled into the sampled gas stream to produce a 10 fold increase in SO_2 concentration thereby simulating the worst case condition with respect to SO_2 content, such as might be experienced in the combustion of very high sulfur content fuels.

The experimental plan called for analysis of the collected samples for evidence of false particulate formation. If any unexplainable trends were noted, additional well controlled laboratory experiments were contemplated for studying possible mechanisms involved in false particulate formation.

2. Method 5 Parameter Evaluation

To permit a critical review of the applicability of Method 5 as written for oil-fired steam generators, a statistically designed set of experiments was developed to examine several procedural steps (factors), each at two levels. After discussions with the other contractor and the EPA Project Officer, it was mutually agreed to evaluate nozzle type, filter diameter and filter temperature. Independent evaluations of these three factors at two levels requires a total of 2^3 or 8 combinations, as follows:

		N_1	N_2
F_1	T_1	X	X
	T_2	X	X
F_2	T_1	X	X
	T_2	X	X

where

X = samples to be collected
T = filter temperature (T_1 = 120°C, T_2 = stack temperature)
F = filter diameter (F_1 = 6.3 cm [2-1/2"], F_2 = 10 cm [4"])
N = nozzle type (N_1 = button hook; N_2 = 90° bend)

The experimental design was based upon simultaneous collection of two samples, with each pair of simultaneous measurements comprising a "block." For this purpose, identical Method 5 sampling trains were employed, varied only with respect to nozzle type and filter size according to the experiment plan. The A train sampling was carried out in Port S1 (Figure 2). To maximize the amount of information available from this series of tests, it was decided to employ three replicates; separate test factors were confounded with blocks within each replicate so that information would be available to study both main effects and first order interaction effects. The experimental design is given in Table 2.

TABLE 4

EXPERIMENTAL DESIGN FOR STUDY OF FILTER SIZE, FILTER TEMPERATURE AND NOZZLE TYPE

			A TRAIN			B TRAIN		
Replicate	Block	Order of Test	Filter Size	Temp	Nozzle	Filter Size	Temp	Nozzle
I	1	2	6.3cm	120°C	BH	6.3cm	stack	90
	2	4	10	stack	90	10	120°C	BH
	3	7	6.3	stack	BH	6.3	120	90
	4	5	10	120	90	10	stack	BH
II	5	8	10	120	90	6.3	120	BH
	6	9	10	120	90	6.3	120	90
	7	11	6.3	stack	BH	10	stack	90
	8	1	10	stack	BH	6.3	stack	90
III	9	12	6.3	120	BH	10	stack	BH
	10	6	10	120	BH	6.3	stack	BH
	11	10	10	stack	90	6.3	120	90
	12	3	6.3	stack	90	10	120	90

the order of sample collection by blocks was randomized as a means of minimizing the influence from any variation in source conditions. Furthermore, it was assumed that Systems A and B were equivalent with respect to source stream conditions as well as sampling and cleanup protocols.

The basis for this design is the analysis by variance technique, which assumes that the observations are random variables with well defined distributional properties. Utilizing the particulate catch data for all 24 experimental runs, the variance in result can be independently determined for replicates, blocks, each of the main effects, interaction effects and experimental uncertainty (error). The value of the ratio of any of the above terms to the experimental error permits one to test the hypothesis that the term considered has no influence on weight collected. If the hypothesis is rejected, one can conclude that different levels of the term lead to a significant difference in the amount of collected particulate.

3. Laboratory Studies

In addition to the field experiments described above, several laboratory studies were conducted to evaluate specific Method 5 criteria and to provide guidance in improving sampling procedures for the second set of field samples. The first of these independent studies included a measurement of internal and external temperatures along the front half of the sampling system for several stream conditions. The purpose of this study was to determine the most reliable reference point for controlling probe and filter box heaters to maintain a gas temperature of 120°C at the back of the probe and at the filter. A second study involved an evaluation of the usability of several instack filter holders and the physical and thermal properties of various filter media employed in these holders. The results of these studies are presented in separate reports.*

B. Sample Collection

The sampling plan followed throughout all runs called for the simultaneous collection of samples with A and B trains from points of essentially identical stream conditions; Ports A51 and A52 (Figure 2) were utilized, with sampling points being approximately 90 cm within the ductwork and 15 cm apart. Except as previously mentioned, sampling was conducted according to the Method 5 procedure, with the train configuration being adapted to accommodate the desired experiment. An impinger train was utilized in all runs. Besides permitting a measurement of the moisture content of the stream, the impinger solutions were occasionally dried down to yield the "back half" particulate level. Throughout the first

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*E.T. Peters and J.W. Adams, "The Measurement and Control of Gas Temperature in a Method 5 Sampling Train," Special Report, EPA Contract 68-02-0632, in preparation.

E.T. Peters, J.W. Adams and A.L. Benson, "Properties of Several In-stack Filters and Filter Holders for Source Sampling," Special Report, EPA Contract 68-02-0632, in preparation.

set of experiments, the impingers were charged with 10% H_2O_2 in 0.1N NaOH (prepared fresh before each run) to scrub out SO_2. The impinger solutions were subsequently analyzed for sulfate, providing a measure of total SO_x for comparison to the SO_2-SO_3 train results. For the second set of experiments, the impingers were charged with distilled water.

Sampling duration was typically one to two hours for the first set of runs and one hour for experiments in the second evaluation. Sampling was isokinetic, except for those cases where particular train components being utilized resulted in an excessive pressure drop across the system. For these cases, both trains were operated at the same lower-than-isokinetic rate.

Stack velocity, pressure and temperature measurements were made at frequent intervals during the course of sampling. System temperatures were initially monitored and controlled from convenient external reference points. However, based on the results of a laboratory investigation of exit gas temperature as a function of various reference control positions (separately reported), an internal reference point was utilized for controlling system temperatures during the second set of experiments.

Concurrent with the initial set of experiments, an SO_2-SO_3 sample was withdrawn from port AE (Fig. 2). Separate values for SO_2 and SO_3 concentrations were obtained by EPA Method 8 and the barium chloranilate procedure for analysis of sulfate. In addition, an Orsat sample was obtained during each experiment to determine flue gas composition.

After sampling, the particulate catch was separated into several fractions, as described previously. For experiments utilizing an instack filter, the samples were identified by the code given in Figure 1A; for Method 5-type runs where only external filters were used, sample coding is described by Figure 1B. In every case, the probe was scrubbed with a nylon brush with several distilled water and acetone rinses. The silica gel and impinger solutions were quantitatively recovered and retained for a subsequent determination of moisture and additional measurements such as sulfate and acidity. All samples were stored in polyethylene bottles.

C. Sample Analysis

Gravimetric determinations of all filter and probe catches were performed after evaporation to dryness and equilibration over a desiccant. To determine if relative humidity had an influence on the magnitude of the particulate catch, weighings of initial samples were made after a 24-hour desiccation over Drierite and again after an additional 24-hour desiccation over P_2O_5. No differences were observed for the two desiccants, and the more convenient Drierite was used for the remainder of the runs.

To lessen the effect of any weighing error on final results, repetitive weighings were performed on all samples. If weighings agreed within 1 mg, the average value was used. If differences of more than 1 mg were found, additional determinations of weight were made by other analysts, with the average taken as the true value.

For experiments conducted within the first set, sulfate and free acid analyses were carried out on all probe, nozzle and filter residues. Initial attempts to use a carbonate fusion led to high blank values and nonreproducible results. Finally, it was demonstrated that a 30-minute leach in 25 ml of hot water completely dissolved all sulfate detectable (as sulfur) by x-ray fluorescence (XRF). By the use of known concentration standards, XRF detection levels were found to be about 0.5 mg SO_4 under the conditions of the filter leaching experiments. Leached solutions were analyzed for sulfate by means of the barium chloranilate colorimetric procedure. Total SO_4 data were obtained from impinger solutions by the chloranilate procedure. Acidity was determined in the leachants by titration with 0.01N NaOH to a phenopthalein end point. No difficulty was encountered in the end point determination for these samples even though past experience has shown that samples containing high Ni or V content could result in interference. Occasionally, particulate samples were analyzed by x-ray fluorescence and emission spectrographic methods to determine the presence and relative concentrations of cation species. X-ray diffraction analyses were attempted in a few cases, but results were inconclusive.

During the second set of experiments, residue samples were occasionally analyzed by one or more of the above techniques to provide information on the sulfate distribution within the sample fractions and to provide qualitative descriptions of the elemental chemistry of various residue samples.

IV. EXPERIMENTAL RESULTS

A total of 30 paired particulate runs were performed at the oil-fired boiler, 18 in response to evaluations of false particulate generation and 12 with respect to the statistical sampling parameter grid. Within the first set, 14 runs were conducted according to the mutually agreed upon design (presented in Section III, A, 1) involving selected variations in sampling time, filter temperature and filter media; SO_2 and SO_3 analyses were conducted concurrently. The sequence of runs with respect to the experimental design is summarized by run no. as follows:

		L = 60 min	L = 120 min
F = 1106 BH	T = 120°C	(1)	(4),11† 12
	T = 150°C	17	13
F = MOF	T = 120°C	(3,6), 8†	(2,5), 7
	T = 150°C	16†	9

( ) - A train data invalid due to leak in sampling system

* - A train data incomplete due to loss of sample APE

† - Time was increased to 90 minutes to increase the collected mass of sample.

Tables 3 through 6 present the sample collection conditions, SO_2 and SO_3 concentrations in the gas stream, particulate distributions and sulfate distributions, respectively, for these runs. Four additional experimental runs were performed to explore specific opportunities for SO_2 oxidation. Comparable data for these experiments is presented in Tables 7 through 10.

During the initial runs, it was determined that isokinetic sampling was not feasible due to the relatively high stack gas velocity and a substantial pressure drop across the system equipped with an instack filter. As a result, it was decided to sample equivalently with both systems at rates below isokinetic. This deviation from the Method 5 procedure was justified by the following points--results were interpreted on the basis of a relative comparison of the particulate catch from the two trains, very little influence on particulate loadings would result from the predominately submicron size particulate in the gas stream, and lower rates permitted longer sampling times thus tending to smooth out short term source fluctuations.

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TABLE 3

SAMPLING CONDITIONS FOR SET I EXPERIMENTAL GRID

Run Number	Filter Temp (°C)	Filter Type*	Date	Stack Temp (°C)	Run Time (min)	Moisture Content (%)	Gas Volume Collected (m^3)
1A	120	1106	4-16-73	150	60	4.1	0.685
B					60	12.3	0.909
2A	120	MQF		150	120	4.5	1.693
B					120	11.8	1.811
3A	110	MQF	4-24-73	145	60	4.1	1.107
B					60	11.9	1.309
4A	120	1106		145	120	7.5	2.461
B					120	12.0	2.498
5A	120	MQF	4-25-73	135	120	6.5	1.651
B					120	11.0	1.820
6A	120	MQF		130	60	9.8	0.846
B					60	11.1	0.911
7A	120	MQF	5-01-73	145	135	11.5	1.929
B					135	11.7	2.033
8A	120	MQF		145	90	11.5	1.326
B					90	11.8	1.453
9A	145	MQF	5-02-73	145	120	12.0	1.568
B					120	12.2	1.661
10A	145	MQF		145	90	12.6	1.306
B					90	12.7	1.352
11A	120	1106	5-08-73	145	109	12.1	1.626
B					113	12.2	1.750
12A	120	1106		145	108	12.3	1.550
B					109	12.4	1.652
13A	150	1106	5-10-73	145	125	11.3	1.701
B					114	11.6	1.746
17A	150	1106	5-17-73	140	60	12.6	0.890
B					60	12.8	0.928

* 1106 - MSA Type 1106 BH Glass Fiber Filter
MQF - Pallflex "Tissuequartz" Filter with a strengthening treatment applied by Arthur D. Little, Inc.

TABLE 4

SULFUR OXIDES IN STACK GAS FOR SET 1 EXPERIMENT GRID*

Run Number	Particulate Trains SO_2 (Impinger) (mg $SO_4^=/m^3$)		SO_x Train SO_2 (mg $SO_4^=/m^3$)	SO_3 (mg $SO_4^=/m^3$)
	A-Train	B-Train		
1	NA †	1050	965	5.9
2	NA	1030	1300	5.7
3	NA	1000	1250	2.1
4	NA	630	1050	1.4
5	NA	670	875	8.3
6	NA	870	875	7.9
7	870	900	860	2.9
8	760	870	960	0.6
9	900	990	815	1.3
10	990	860	530	0.9
11	910	900	870	3.7
12	860	920	890	5.6
13	820	850	880	1.9
17	830	800	---	1.7
Average (All Runs)	865	880	790	3.6
Average (Runs 7-17)	875		870	2.3

* 4 mg $SO_4^=$ as 1 ppm SO_2 or SO_3
† not analyzed

TABLE 5

[redacted]

Run No.	Particulate Mass (μg/m³)									[redacted]	[redacted]
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]		
1							30	26	56		
2							15	26	41		
3							25	22	47		
4							12	24	36		
5							10	17	27		
6							27	17	38		
7	75	60	5	2	75	62	44	25	69	0.52	0.80
8	71	48	6	1	59	66	39	23	52	1.05	0.94
9	74	63	2	3	77	62	52	30	81	1.05	0.95
10	8	52	3	–	61	64	41	23	64	1.05	1.00
11	–	28	5	–	–	–	15	27	42	–	–
12	8	69	1	0	77	78	37	41	78	1.01	1.00
13	4	17	2	1	27	24	9	23	32	1.52	1.33
17	8	25	1	5	33	39	18	24	42	1.27	1.08
Avg [1-12]					59	62			61	1.05	0.98
Avg All										1.02	1.03

+ SP = [redacted] = [redacted] —[redacted] was lost.

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TABLE 6

SULFATE ($SO_4^=$) DISTRIBUTIONS IN SET 1 EXPERIMENT GRID SAMPLES

Run Number	Sulfate Mass -- mg/m^3									B/A*	B/A
	APS	AFS	APE	AFE	A*[1]	A-Total	BP	BF	B-Total		
7	5	21	2	0	26	28	15	11	26	1.00	0.93
8	4	15	2	0	19	21	13	10	23	1.21	1.09
9	4	29	0	0	33	33	11	10	21	0.64	0.64
10	2	19	1	0	21	22	16	10	26	1.19	1.14
12	3	23	1	0	26	27	20	13	33	1.27	1.22
13	2	9	0	1	11	12	5	10	15	1.18	1.08
17	2	9	1	1	11	13	8	15	23	2.09	1.77
Average (7-17)					21	22			23	1.10	1.05
Average (A/B)										1.23	1.12

[1] A* = APS+AFS

TABLE 7

SAMPLING CONDITIONS FOR ADDITIONAL SET 1 EXPERIMENTS

Run Number	Filter Temp (°C)	Filter Type*	Date	Stack Temp (°C)	Run Time (min)	Moisture Content (%)	Gas Volume Collected (m^3)
A. SO_2 Enrichment (~2000 ppm SO_2)							
15 A			5-15-73	140	129	9.1	1.83
B	110	1106			129	10.0	1.97
B. Both Trains Run As EPA Method 5 Trains							
1. Influence of Soiled Probe (Probe was not cleaned between Runs 14 and 14')							
14 B1	120	MQF	5-10-73	145	60	11.9	1.17
B2	120	1106			60	11.7	1.11
14' B1	120	MQF	5-10-73	145	90	11.9	1.36
B2	120	1106			90	11.7	1.37
2. Influence of SO_2 Enrichment (B2 spiked for ~2000 ppm SO_2 in sampled gas)							
16 B1	125	MQF	5-17-73	140	120	12.1	1.75
B2	120	MQF			120	10.8	1.78
3. Influence of SO_2 on Soiled Filter (B2 contained a soiled filter behind the regular filter, trains were spiked for ~2000 ppm SO_2 in sampled gas).							
18 B1	120	MQF	5-18-73	130	120	9.4	1.72
B2	120	MQF			120	9.7	1.80

* 1106 - MSA Type 1106 BH Glass Fiber Filter
MQF - Pallflex "Tissuequartz" Filter with a strengthening Treatment Applied by Arthur D. Little, Inc.

TABLE 8

SULFUR OXIDES IN STACK GAS FOR ADDITIONAL SET 1 EXPERIMENTS*

Run Number	Particulate Trains SO_2 (impinger) (mg $SO_4^=/m^3$)		SO_2 Train	
	A-Train	B-Train	SO_2 (mg $SO_4^=/m^3$)	SO_3 (mg $SO_4^=/m^3$)
14+14'	----	----	660	1.9
15	8120	6780	---	2.9
16	730	1930	---	2.7
18	8530	6160	---	2.8

* 4 mg $SO_4^=$ = 1 ppm SO_2 or SO_3

TABLE 9

MASS DISTRIBUTIONS IN ADDITIONAL SET 1 EXPERIMENT SAMPLES

Run No.	Particulate Mass - mg/m³									B/A*	B/A
	APS	AFS	APE	AFE	A*†	A-Total	BP	BE	B-Total		
15	10	35	2	0	45	47	30	33	63	1.40	1.34
14-1							--	15	--		
-2							--	21	--		
14'-1							23	26	64††		
-2							28	33	62††	B1/B2 = 0.78	
16-1							21	17	38		
16-2							18	13	31	B1/B2 = 1.22	
13-1							18	12	30		
16-2							14	12	26	B1/B2 = 1.15	

†A* = APS + AFS

††Total for Runs 14 and 14'

TABLE 16

SULFATE ($SO_4^{=}$) DISTRIBUTIONS IN ADDITIONAL SET 1 EXPERIMENT SAMPLES

Run Number	Sulfate Mass — mg/m^3									B/F*	B/A
	APS	ACS	AFC	AFC	A**	A-Total	BP	BF	B-Total		
15	4	3	1	4	7	12	12	2	14	2.00	1.17
15A-1							18	—	—		
15A-2							12	—	—		
16-1							8	9	17	B1/B2 = 1.30	
16-2							6	7	13		
18-1							4	5	9	B1/B2 = 0.45	
18-2							5	15**	20		

B = APS + ACS

**Includes sulfate on scalped filter (Run 14*)

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The data presented for the A train, Runs 1 through 6, were influenced by a leak between the instack filter and probe assemblies, allowing the collected sample to be diluted by ambient air. Thus, the particulate catches for these runs were biased to the low side. Progressive steps were taken in the field to correct this problem, with improved results for Runs 4 and 5 and even greater improvement for Run 6. An approximate measure of the ambient air dilution can be estimated from the observed moisture content of the stack gases; on this basis, the dilution factor was about 200% for Runs 1-3, 70% for Runs 4 and 5 and 10% for Run 6. Because of the magnitude of correction necessary, no correlation was attempted between the A train and B train for these runs.

Concurrent with the initial 18 particulate samples, Orsat and SO_3 samples were obtained from Port AE (see Figure 2). The SO_3 sample was withdrawn through a specially designed Method 8 train, selectively condensing SO_3 prior to scrubbing out SO_2 in a 10% H_2O_2 solution. Condensor washings and impinger solutions were segregated and retained for verium chloranilate colorimetric analysis. Stack gas compositions determined by Orsat analysis of a gas sample withdrawn from Port AE were found to agree with the results obtained from samples routinely collected by station personnel at a point just above the economizer. Typical values were 12-14% CO_2 and 1-3% O_2.

A few additional analyses were conducted on the particulate on occasion to provide some understanding of the distribution and concentration of cation species. Optical emission spectrographic and x-ray fluorescence analysis results for several samples is provided in Table 11.

Twelve paired samples were obtained during the second evaluation; data regarding sampling collection conditions and measured values of particulate distributions are presented in Table 12 and 13. Experimentally, no difficulties were encountered during this latter investigation, excepting the necessity to conduct two runs at approximately 70% of the isokinetic condition. Both trains were operated equivalently.

The first set of experiments (Runs 1-18) had been carried out with the probe liner temperature at the back of the probe maintained at 120°C. In the interim between the first and second sets of experiments, a separate laboratory evaluation was made of gas temperature versus external system temperature at several positions along a Method 5 sampling train as a function of variations in stream condition. It was determined that for sampling conditions similar to those employed in the field the externally measured temperatures at the back of the probe could be 25°C or more colder than the gas temperature at this point. As a result, the second set of experiments utilized an internal reference thermocouple at the back of the probe. The output of this thermocouple was fed to a proportional controller for the probe heater, set to maintain a gas temperature of either 120°C or stack temperature (160°C). The filter box temperature was maintained at 120±10°C. Because of the difference in

TABLE II

CHEMICAL ANALYSIS OF COLLECTED PARTICULATE

A. Optical Emission Spectroscopy (Qualitative)

Concentration	SAMPLES						
	SAFS	SAFE	SBF	BAPS	BAPE	BBP	TCBP
> 10%	-	-	-	-	-	Mg	Mg
3-30	Mg	-	-	-	-	V	V
1-10	V	-	Mg	-	-	Fe	Fe
0.3-3	Ni	-	Ni,V	Fe	Fe	Ni,Si	Ni,Si
0.1-1	-	-	-	Mg	-	Al,Zn	Al,Zn

B. X-ray Fluorescence (Qualitative)[a]

Amount	SAMPLES		
	SAFS	SAFE	NBF
Strong	S,V	-	S,V
Medium	K,Ni,Fe	-	Ni,K,Fe
Weak	Pb	-	Pb
Trace	-	Pb,S	-

[a] Mg cannot be analyzed by the apparatus employed

TABLE 13

MASS DISTRIBUTIONS IN SET 2 EXPERIMENTAL GRID SAMPLES

Run No.	Particulate Mass (mg/m^3)					
	AP	AF	ATotal	BP	BF	BTotal
39	14	18	32	29	18	47
40	12	23	35	22	24	46
41	13	20	33	10	23	33
42	9	19	28	9	17	26
43	9	15	24	9	12	21
44	7	18	25	13	17	30
45	9	18	27	8	18	26
46	29	25	54	10	20	30
47	11	26	37	11	24	35
48	9	22	31	23	16	39
49	8	14	22	8	16	24
50	10	16	26	9	18	27

gas temperature at the back of the probe for the two sets of experiments (estimated to be 150-160°C for the first set versus 120°C for the second set), several samples from the second set were analyzed to obtain sulfate distributions for comparison to the values obtained in the first set. In this way, it was hoped to determine if a higher gas temperature in the probe resulted in less condensation of SO_3 or conversely provided improved kinetics for SO_2 conversion to sulfate. The results are given in Table 14.

Finally, five pairs of samples were collected in which one train was operated by the Method 5 procedure and the other train employed either an in-stack particulate collector or an external flat quartz filter. These runs were performed as an extension of a laboratory study concerned with evaluating the usability of various instack collectors and filter media. The results of these experiments are described in a separate report. However, so that all test data for this oil-fired utility boiler are together in one report, the sampling conditions and particulate distributions obtained for these five experiments are included in Tables 15 and 16, respectively.

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TABLE 14

SULFATE ($SO_4^=$) DISTRIBUTIONS IN SELECTED SET 2 EXPERIMENT GRID SAMPLES AND COMPARISON TO SET 1 EXPERIMENT GRID SAMPLES

A. Set 2 Data (Buttonhook nozzle, 2-1/2" filter)

Filter Temp	Run No.	Mass of Sulfate (mg/m^3)		Percent Sulfate/ Total Particulate	
		F	F	F	F
120°C	40A	1	5	4	28
	46B	2	9	18	43
	50A	2	12	18	71
150°C	44B	2	12	17	71
	45A	2	10	25	54
	49A	2	11	24	80

B. Comparison of Average Results

Probe Temp*	Filter Temp	Tests	Mass of Sulfate (mg/m^3)		Percent Sulfate/ Total Particulate	
Set 1			F	F	F	F
~150°C	120°C	6	11	10	33	37
	150°C	4	10	11	36	43
Set 2						
120°C	120°C	3	2	9	13	47
	150°C	3	2	11	22	68

*Gas temperature at the back of the probe

TABLE 15

SAMPLING CONDITIONS FOR ADDITIONAL FIELD TESTS IN SUPPORT OF LABORATORY EVALUATIONS

Run Number	Experiment Description	Date	Stack temperature (°C)	Run Time (min)	Moisture Content (%)	Average stack Velocity m/sec	Gas Volume (m³) collected (actual conditions)	Gas Volume (m³) collected (standard conditions)	Average sample Velocity m/sec	Isokinetic (%) Average
33A	In-stack thimble	6-26-74	155	60	11.9	25.23	1.780	1.902	25.61	101.5
B	10 cm external filter MSA-1106-BH			60	12.1	25.23	1.804	1.956	25.73	102.0
34A	In-stack thimble	6-27-74	155	60	9.1	25.25	1.785	1.947	25.20	99.8
B	10 cm external filter MSA-1106-BH			60	9.6	25.25	1.793	1.884	25.85	99.2
35A	In-stack thimble	6-27-74	150	60	10.8	24.77	1.850	2.079	26.57	107.2
B	10 cm external filter MSA-1106-BH			60	10.7	24.77	1.795	1.977	25.35	102.4
37A	10 cm external filter	6-28-74	150	60	11.3	24.96	1.768	1.964	25.74	103.1
B	10 cm external filter MSA-1106-BH			60	11.5	24.83	1.773	1.952	25.46	102.5
38A	10 cm external filter	6-28-74	150	60	11.2	25.64	1.821	2.015	25.34	102.9
B	10 cm external filter MSA-1106-BH			60	11.5	25.64	1.838	2.032	25.80	101.8

*Svenska Flakt Jobrikon (Sweden) Thimble distributed in the United States by Carborundum Environmental Systems, Inc., Knoxville, Tenn.

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V. DISCUSSION OF RESULTS

A. Set 1 - Generation of False Particulate

1. Experimental Grid (Runs 1-13, 17)

Simultaneous sampling was carried out with a Method 5 train (Train B) and a comparative research train (Train A) employing an in-stack filter. The results of concurrent measurements of SO_2-SO_3 concentrations in the stack gas compared to SO_2 measurements based upon analysis of impinger scrubber solutions from the particulate trains yielded average SO_2 values of ~160 and ~220 ppm, respectively. The difference in result of approximately 30 percent cannot be explained. Separate laboratory evaluations of the collection efficiency of 10% H_2O_2 yielded greater than 90 percent recoveries for conditions simulating the field tests. The calculated concentration of SO_2 for stiochiometric combustion of 0.5 percent sulfur fuel corresponds to 165 ppm (or 130 ppm at 30 percent excess air). Because of these uncertainties, it is necessary to say that typical SO_x levels for this source are within 20 percent of 200 ppm, with SO_3 comprising about 1 percent of the total.

Train B particulate, designated B-total (or B), included the nozzle and probe washings residue and the filter catch. For Train A, the particulate catch was categorized in two ways. The catch designated A* included particulate collected in the nozzle and by the in-stack filter. The catch designated A-total (or A) also included the weight of the dried-down residue from the probe washings and the catch on the external filter, both ostensibly due to condensation of vapor species and penetration of any particulate through the in-stack collector. Train A was used as the control to indicate source variations and was therefore always run according to the same procedure. Three collection times were utilized, yielding the following results:

Sampling Time (min)	Tests	Catch-mg/m^3		Ratio
		A*	A	A*/A
60	1	33	39	0.85
90	2	60	65	0.92
120	4	66	70	0.94

It is observed that 4-6mg of particulate are collected behind the in-stack filter, corresponding to less than 10 percent of the total catch. This amount is not considered significant. The increase in particulate catch with time is attributed to random variations in source emission levels rather than false particulate formation on the in-stack collector.

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Total particulate and sulfate values obtained during concurrent sampling with A and B trains are compared on the basis of B/A* and B/A-total ratios as well as on the combined average results for the seven valid paired runs. These comparative values have been presented earlier in Tables 5 and 6; the average results are repeated here for convenience.

Particulate - mg/m^3 (Average of 7 runs)

	A*	A-Total	B-Total	B/A*	B/A
Total Particulate	58	62	61	1.05	0.98
Sulfate	21	22	23	1.10	1.05
Sulfate/Total Part.	0.38	0.37	0.40	--	--

These average results indicate a near equivalence between the A and B trains; furthermore, about 95% of the total particulate and sulfate is collected in the in-stack section of the A train.

A detailed summary of the distribution of particulate and sulfate as well as sulfate/total particulate ratios is given in Table 17 as a function of collection point within the sampling trains. The average distributions for particulate and for sulfate are almost identical for the two trains, with equivalent scatter in the particulate and sulfate data as indicated by similar values for the coefficient of variation (c.v.). The average ratio of sulfate/total particulate is 0.38 for A train experiments compared to 0.40 for B train experiments--a remarkably close agreement. An especially uniform trend in the sulfate/particulate ratio exists for the nozzle, probe and filter samples for both trains. No data are reported in this table for the AFT sample fraction due to its very small amount (<1 mg), which could result in large sulfate/particulate variations on a percentage basis; on the average, this fraction accounts for only about 3 percent of the total particulate catch (and 1 percent of the total sulfate).

Identical sampling procedures and conditions were employed for collecting all the A train data. The spread in results shown in Table 17, therefore, reflects the level of variation to be expected in repetitive sampling. The fact that values for the coefficient of variation are approximately the same for A and B trains implies that there is no major influence on the B train data as a result of differences in test conditions according to the experimental grid. Likewise, the rather constant sulfate/total particulate ratio of ~0.40 for all sample collection points within both the A and B trains precludes the generation of false sulfate particulate as a result of sampling configuration.

The total particulate and total sulfate collected by the A* and A-total sections of the A train are compared to B train values in Figures 3 and 4, respectively. Excellent correlation to a straight line fit is obtained for B versus A* particulate values, with a coefficient of 0.98. Regression

TABLE 17

COMPARISON OF A TRAIN VERSUS B TRAIN PARTICULATE MASS AND SULFATE DISTRIBUTIONS

RUN NO.	APS	AFS	APE	AFE	A*	A-TOTAL	BP	BF	B-TOTAL
A. PARTICULATE / TOTAL PARTICULATE (%)									
7	18	74	6	2	97		64	36	
8	17	72	9	2	89		63	37	
9	17	78	2	3	95		63	37	
10	12	83	5	0	95		64	36	
12	11	86	1	0	99		44	56	
13	16	72	8	4	88		23	77	
17	20	65	4	11	85		42	58	
Average	16	76	5	3	92		52	48	
c.v.(%)	20	10	59	120	5		31	23	
B. $SO_4^=$ / TOTAL $SO_4^=$ (%)									
7	18	77	5	0	95		58	42	
8	19	74	7	0	93		58	42	
9	13	86	1	0	99		63	37	
10	9	88	2	1	97		62	38	
12	10	86	3	1	96		61	39	
13	13	79	3	5	92		22	78	
17	19	72	5	4	91		35	65	
Average	14	80	4	2	95		51	49	
c.v.(%)	29	8	55	131	3		31	33	

TABLE 17 (Cont'd)

RUN NO.	APS	AFS	APE	AFE	A*	A-TOTAL	BP	BF	B-TOTAL
C.	$SO_4^=$ PARTICULATE								
7	33	35	29	--	35	33	33	43	37
8	36	31	26	--	32	31	33	41	36
9	30	46	19	--	43	42	33	33	33
10	24	36	17	--	34	34	37	41	38
12	33	33	9	--	34	34	64	31	42
13	39	64	21	--	62	60	30	41	43
17	32	38	43	--	33	34	44	59	53
Average	32	39	23	--	38	37	38	41	40
c.v.(%)	16	21	47	--	19	18	27	22	16

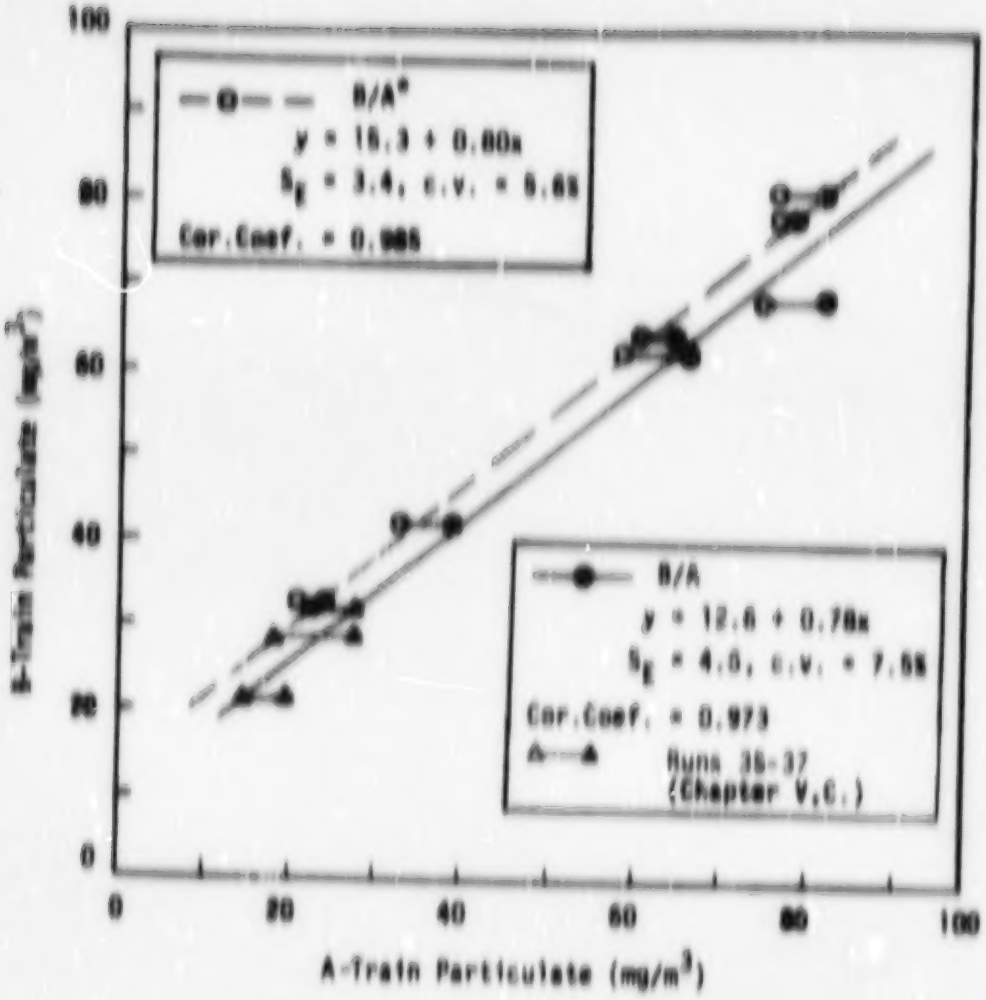

FIGURE 3 Comparison of Particulate Catch A Train Versus B Train

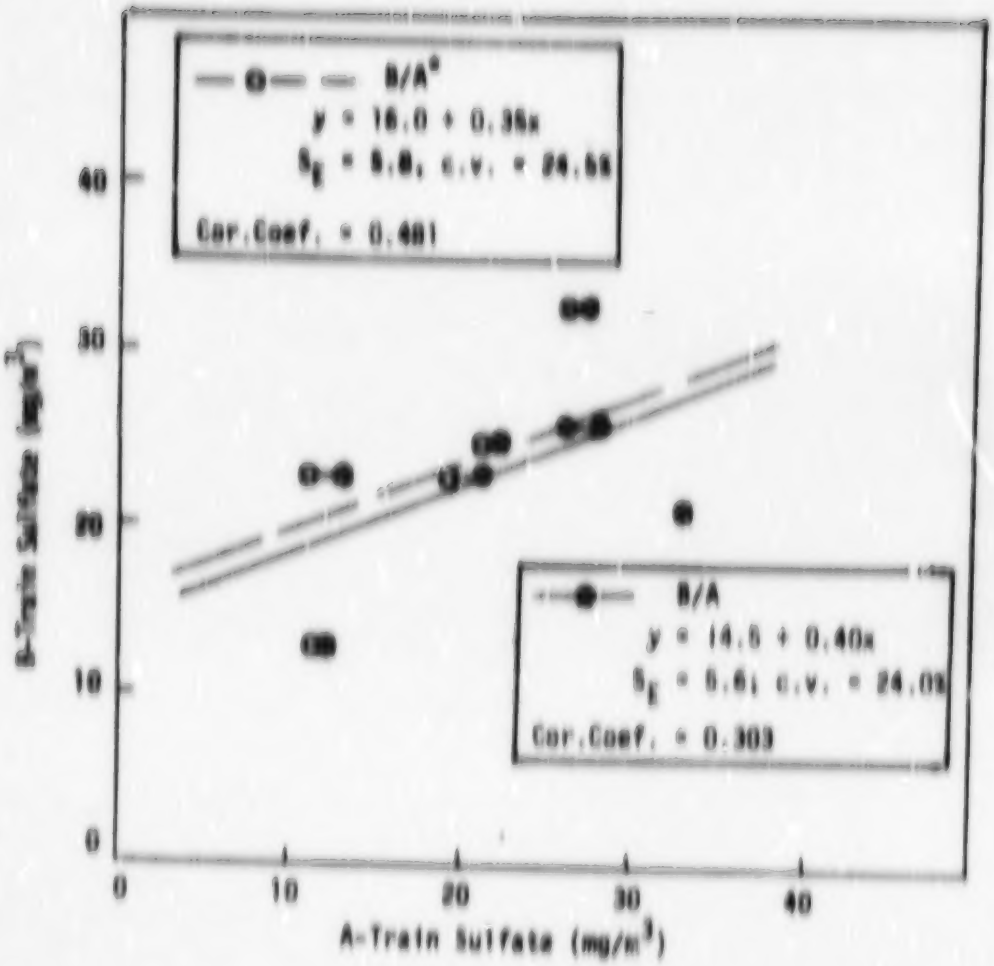

FIGURE 4 Comparison of Sulfate Catch - B Train Versus A Train

analysis yields a slope of 0.80, an intercept of 15 mg and a coefficient of variation corresponding to 6 percent. A similar comparison with Actual values yields comparable results, with a displacement in intercept of about 3 mg. These results imply a background (noise) level of ~15 mg for the B train together with an improvement in collection efficiency for the A train of about 20 percent in comparison to the B train. These two factors result in approximately equal catches for the two trains when loadings are in the range of 60-80 mg/m3. The comparative sulfate data presented in Figure 4 provide similar results. A much larger scatter in the data reduces the confidence in making a linear fit. The results, however, indicate a B train noise level of perhaps as much as 10 mg.

The indication of substantial blank value for the B train suggests a difference in A and B train collection (or sample recovery) characteristics independent of the experimental grid variations in collection time and external filter media and temperature. A possible explanation is the difficulty in obtaining a quantitative recovery from the probe. Independent laboratory studies conducted at ADL have shown that successive washings of a probe liner previously employed for several Method 5 stack tests each continue to provide indicated catches of 5 to 15 mg even after four clean-ups by the Method 5 procedure. IR analysis of these blank residues indicates the presence of considerable sulfate and x-ray fluorescence analysis shows, in addition to large amounts of S, the presence of Ca, K and Si, all typical components of flyash. Thus, the empirical evidence is that glass probes employed for stack sampling (of fossil-fuel boilers) become degraded through some unknown mechanism such that successive probe clean-ups by the EPA procedure yield catches of 5 to 15 mg, much of which is sulfate. This leads to an additional 5 to 15 mg being collected during a Method 5 test that would not be present for a new, non-degraded probe.

The experimental data also indicate that the in-stack section of the A train collects approximately 20 percent more particulate than the B train, based upon the observed least square slope of 0.80. This difference does not appear to be due to "false particulate" generation, for the result is the same irrespective of B train filter temperature, media or sampling time. A reasonable explanation is incomplete recovery and measurement of the actual particulate burden to the probe. Opportunities are available for particulate loss during probe washing, recovery from sample bottles and solution dry down to a residue. It is not unreasonable to suggest that incomplete sample recovery from the probe results in as much as a 20 percent reduction in total measured particulate.

The elemental chemistry of the various samples from trains A and B is rather uniform, as shown by the analytical data presented in Table II. The optical emission spectroscopy (OES) was carried out on residue from a hot water extraction combined with ultrasonic agitation of the filter samples and directly on the residues from the probe washings. The XRF analyses were performed directly on the filters. All of the detected elements are expected for this type of source. Mg and Al are present as solids in the scaling additive, and Ni, V and Fe are the major

metallic impurities in the fuel; sulfur, of course, is the major non-metallic impurity in the oil. Most of the sulfur in the collected particulate is present as $MgSO_4$. The small amount of Pb observed by XRF is associated with the MOF filter, where Pb is present as the major impurity; the Pb is not extracted by a hot water leach and therefore is not observed in the OES analyses. Based upon calibration standards, the trace of S observed on the external filter of Train A (sample 0AFE) corresponds to less than 0.6 mg SO_4 for the entire filter. The close agreement between Train A and B samples and between filter and probe samples tends to discount the presence of any significant amount of inorganic "false particulate."

In summary, for the particular source tested, there has been no indication of any "false particulate" being formed as a result of variation in filter media, external filter temperature or level of loading (sampling time). However, it can be argued that this facility discharges a "clean" emission stream (nominally 200 ppm SO_2, 1-2 ppm SO_3 and ~0.04 grains/m^3) and is not representative of oil-fired utility boilers in general. To address this point, several additional experiments were conducted to simulate high sulfur fuel combustion, thereby improving the opportunity for forming "false particulate." These experiments are described in the following section.

2. Additional Set 1 Experiments (Runs 14, 15, 16 and 16)

Several additional experiments were carried out under conditions which were expected to maximize the opportunity for false particulate formation in various parts of a sampling train. The results for these experiments have been given in Tables 9 and 10. The results are interpreted as follows:

a. Run 15 (SO_2 enrichment)

Both trains were spiked with SO_2, resulting in a resulting gas stream SO_2 concentration of ~2000 ppm in the A train and ~1500 ppm in the B train. The A train utilized MOF filters, whereas an MSA 1106 filter was utilized in the B train. The data in Tables 9 and 10 show that the B train has collected about 30 percent more particulate and sulfate, respectively, than the A train. However, the sulfate to total particulate ratio is constant at 23 percent for both trains compared to a typical (average) ratio of ~40 percent. The filter media thus does not appear to have an influence on the amount of sulfate collected. It is concluded that there was no conversion of SO_2 to sulfate, i.e., no "false particulate" was formed.

b. Both Trains Run as Method 5 Trains

1. Runs 14 and 14' (two consecutive runs without cleaning probe in between)

The two trains were run in identical fashion except the B1 train utilized MOF filters and the B2 train an 1106 filter. The primary

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purpose of this run was to obtain a supply of soiled filters for utilization in other experiments. Nevertheless, the combined particulate catch for Runs 14 and 14' yielded identical distributions for probe (39%) and filter (65%) catches for both trains. The probe catch of both A and B trains corresponded to 43 percent sulfate, in good agreement to the typical value of 38 percent observed for the experimental grid. These results tend to preclude the formation of "false particulate" by interaction of the sampled gas stream and particulate already collected along the probe. Also, there is apparently no difference in result with either a MSP or an 1106 filter.

2. Run 16 (One train (B2) was enriched with SO_2 (~1000 ppm SO_2 added to the sampled stream) and the other train (B1) was run in the normal manner, with ~200 ppm SO_2 in the stack stream.)

The ratio of sulfate to the total particulate in the probe washings (BP) was slightly higher for the train sampling the enriched stream (46%) than for the normal ~200 ppm SO_2 stream (38%); this difference (corresponding to 3 mg sulfate) is not considered to be significant. The ratio of sulfate to the total particulate in the filter catch (Bf) was the same for both trains (52%). It is of interest to note that 20% more particulate was collected by the normal train than by the train with SO_2 enrichment. It is concluded that there was no conversion of SO_2 to particulate sulfate in a stream containing ~1000 ppm SO_2.

3. Run 18 (Each train utilized a three-deep filter sandwich, with the second filter facing downstream. Train B1 utilized clean filters, whereas Train B2 utilized a filter sandwich consisting of a clean filter, a soiled filter (from Run 14'B1) and a clean filter. The soiled filter was reversed to contact the third filter, with the two being weighed as a unit. SO_2 enrichment was employed to provide gas streams containing ~2000 and ~1500 ppm SO_2 for the two trains, respectively.)

The soiled filter showed no weight gain, precluding SO_2 conversion to particulate on the filter. The two trains yielded comparable results in terms of particulate distributions. Likewise, the clean backup filter in Train B1 did not change in weight, reinforcing the conclusion that there is no SO_2-filter media interaction even with very high SO_2 challenges.

None of these additional tests gave any indication of "false particulate" formation, even under the extreme conditions of very high SO_2 concentrations.

B. Set 2 - Method 5 Parameter Evaluation

A total of 24 experimental conditions were evaluated in order to determine the influence of varying filter size (6.3 and 10 cm), temperature (250° and stack) and nozzle type (button-hook and 90°). Three replications of the 23 = 8 unique combinations were tested according to an experimental pattern based on statistical design principles. The observed weight gains of filter and probe catches, normalized to a volume of 1 m^3, were determined for each test conditions, providing the basis for this analysis.

Three independent measurements were obtained for the probe catch. One of the initial weights for Run 43B appeared to be in error and was deleted. Differences among the three measurements were negligible (in a statistical sense), and these values were averaged for this analysis. As a foreign particle was noted in Run 50A, an overall average probe weight gain was computed from the other 23 observations and inserted as an estimate. The observed values, to be described, are summarized in Table 18 and are presented graphically in Figure 6. The experimental design of the test grid was given earlier in Table 2.

The particulate distribution between the probe and filter is presented in Figure 6. The data show that, on the average, 40 percent of the catch is in the probe. This compares to 52 percent found for the Set 1 experimental grid runs.

The normalized values of particulate catch given in Table 18 were analyzed according to a widely used statistical technique known as the "Analysis of Variance." The basic assumption implicit in this technique is that the observations are random variables, with well-defined distributional properties, that can be expressed as an additive function of parameters associated with possible sources of variation under investigation. If appropriate assumptions are satisfied, it is possible to test hypotheses and estimate effects concerning the parameters of interest. For these data, the Analysis of Variance computations are summarized in Table 19. The average (mean) value of the total particulate catch is 31.40 mg/m^3, with a standard error of 4.67 and a coefficient of variation corresponding to 15 percent. For example, under the null hypothesis that there is no difference among the three replicates, the value given for Mean Square (74.75 in this case) is an independent estimate of experimental error mean square. Thus, computed F-values, corresponding to the ratio (Replicate Mean Square/Error Mean Square) can be used to test the hypothesis that the replicates have no effect on weight collected, as the theoretical behavior of this ratio is known if this hypothesis is correct. For these data, this

TABLE 18

SUMMARY OF MEASURED PARTICULATE MASSES
IN SET 2 EXPERIMENTAL GRID SAMPLES

Block	Run No.	Probe Catch (mg/m^3)		Filter Catch (mg/m^3)		Total Catch (mg/m^3)	
		Train A	Train B	Train A	Train B	Train A	Train B
1	40	11.75	21.70	23.15	23.67	34.90	45.37
2	42	9.00	9.06	19.29	17.19	28.29	26.25
3	45	8.48	8.04	17.89	18.44	26.37	26.48
4	43	8.57	8.66	14.93	11.90	23.50	20.56
5	46	20.66	9.99	24.62	20.16	53.30	30.15
6	47	10.63	11.37	25.86	23.51	36.49	34.88
7	49	7.98	7.71	13.60	15.71	21.58	23.42
8	39	14.35	28.75	17.62	18.10	31.97	46.85
9	50	10.02	8.94	16.30	18.30	26.32	27.24
10	44	8.55	13.04	17.72	17.42	24.67	30.46
11	48	8.47	22.33	21.64	16.08	30.31	38.91
12	41	12.96	9.52	19.91	23.09	32.71	32.61

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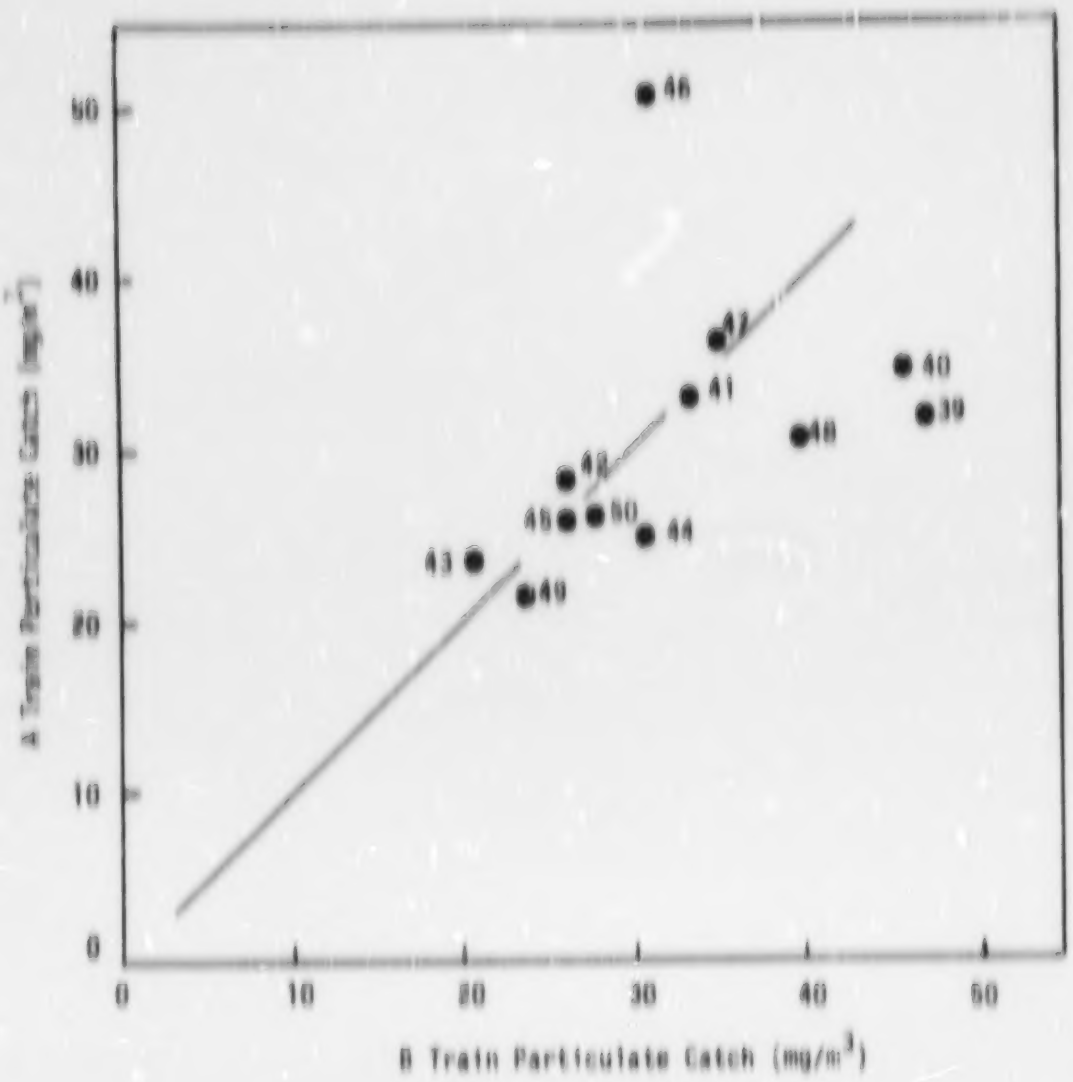

FIGURE 5 Comparison of A Train and B Train Particulate Catches for Set 2 Experimental Grid (Numbers refer to Run No.)

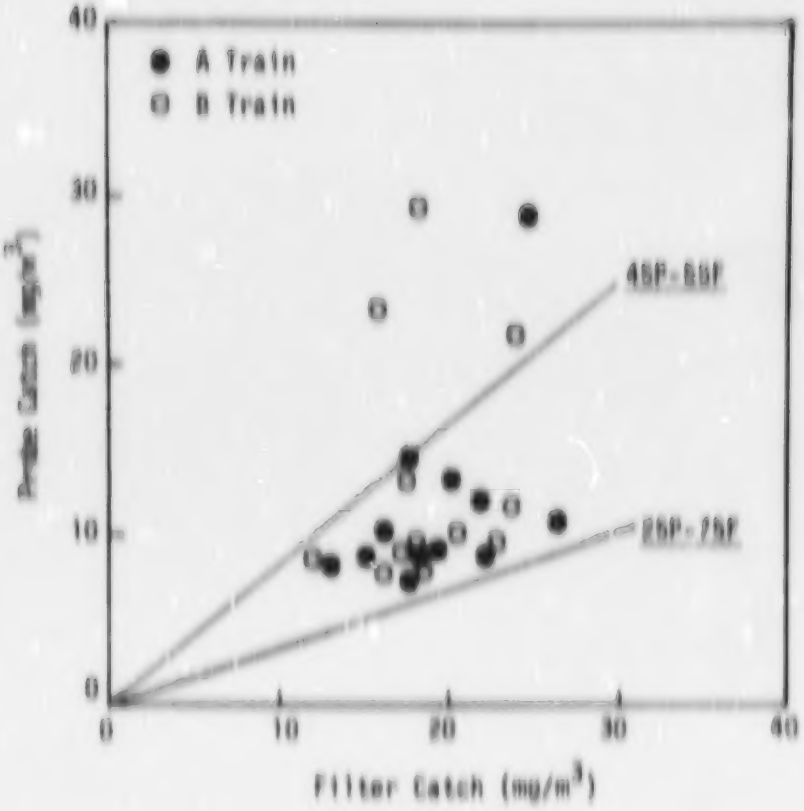

FIGURE 6 Distribution of Particulate Between Probe and Filter for Set 2 Experimental Grid

TABLE 19

ANALYSIS OF VARIANCE TABLE FOR SET A
EXPERIMENTAL GRID SAMPLES: TOTAL PARTICULATE

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Value
Replicates	2	149.49	74.75	3.42
Blocks with reps	9	894.88	99.43	4.55
Filter Size	1	0.21	0.21	0.01
Temperature	1	3.68	3.68	0.17
Nozzle Type	1	181.04	181.04	8.30
Size x Temp Interaction	1	150.43	150.43	6.88
Size x Type Interaction	1	5.56	5.56	0.25
Temp x Type Interaction	1	25.07	25.07	1.14
Experimental Error	6	131.06	21.84	--

hypothesis cannot be rejected and we conclude that there is no measurable difference among the three replicates. This, of course, is a desirable result since the reps were randomly determined, and should not contribute significantly to variations in the data.

Performing similar analyses on the other sources of variation, it was determined that effects due to blocks, nozzle type, and size by temperature interaction were statistically significant.

The significant difference noted among blocks is not surprising since blocks were constructed for the purpose of explaining and estimating these differences. The effect due to changing nozzle type can be estimated from the first two reps only (blocks 1-8), as the contribution in the third rep cannot be disassociated with the block effect, i.e., the same nozzle type was tested in both cells of each block for blocks 9-12. Therefore, the difference in collected particulate for the two nozzle configurations is estimated as follows:

$$\begin{aligned}\text{Nozzle Type Effect} &= (\text{Average of observations in Blocks 1-8 with smooth nozzle}) \\ &\quad - (\text{Average of observations in Blocks 1-8 with BH nozzle}) \\ &= 35.3 - 28.5 \\ &= 6.8 \text{ mg/m}^3\end{aligned}$$

If the observed difference (6.8 mg/m^3 in this case) has a "very unlikely chance" of occurrence when, in fact, there should be no difference, the hypothesis is rejected. For this analysis, the difference of 6.8 (or larger) can be expected to occur with probability less than .05, thus leading to rejection of the hypothesis.

In terms of estimation, the error mean square can be used to compute a 95% confidence interval about the "true" difference between nozzle configurations; namely,

$$\text{Nozzle Type Effect} = 6.8 \pm 1.96 \sqrt{\frac{21.88}{8} \times 2}$$

$$= 6.8 \pm 4.6$$

Thus, there is 95% confidence that the interval 2.2 mg/m^3 to 11.4 mg/m^3 includes the true increase in particulate that the 90° nozzle actually yields over that of the button hook nozzle.

The size x temperature interaction, also declared significant, is illustrated in Figure 7. Again, valid comparisons can be made only from data in blocks 1-8 as this interaction effect is also confounded with blocks in the third replicate. With reference to Figure 7, it is observed that a change in temperature level has a substantially different effect on

TEMPERATURE

FILTER SIZE	Stack	250°
2-1/2"	35.0	31.6
4"	26.1	34.9

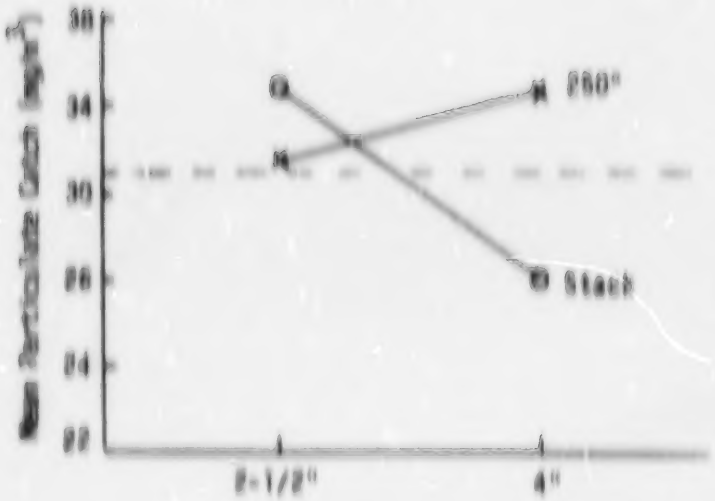

FIGURE 7 Schematic Presentation of the Significant Filter Size-Temperature Interaction Determined by an Analysis of Variance

collected particulate when using a 2-1/2" filter compared to a 4" filter. This mean difference and the 95% confidence interval about this mean difference is 6.1 ± 4.6.

In summary, the analysis of combined filter and probe weight gains has indicated a measurable difference attributable to nozzle type, as well as to the combined filter size-temperature interaction. In an attempt to determine the relative importance of the probe catch and filter catch with respect to the above observations, an Analysis of Variance was also conducted for the filter catch alone. These data are summarized in Table 20. Based upon this analysis, a significant difference is found for the filter size, the nozzle type and the filter size-nozzle type interaction.

The results of this analysis are summarized in Table 21. It is observed that the largest source of random variation is associated with the probe catch, with a coefficient of variation corresponding to almost 40 percent. This compares to about 5 percent for the filter catch and yields a value of 15 percent coefficient of variation for the total particulate. This suggests that it would be highly desirable to avoid particulate collection in the probe as could be accomplished by the use of an in-stack collector. Because of the substantially lower standard error associated with the filter catch data, a more sensitive test can be made for statistical significance among the various effects tested than by using the probe (or total) catch values. Thus, an analysis of variance for the probe data shows three significant effects--filter size, nozzle type and a filter size nozzle type interaction. However, the resulting uncertainty to an emission measurement of 1 to 3 mg out of 30, i.e., 10 percent or less, is acceptable. On the other hand, in utilizing values for the total catch, only two effects are found to be significant--the nozzle type and the filter size temperature interaction. In light of the large confidence interval, however, these result in an uncertainty of anywhere from 5 to 35 percent.

Based upon an analysis of variance, it is concluded that there is substantial experimental scatter associated with the probe catch. Effects found to have significant differences in particulate catch for the levels tested and to also result in a substantial bias to the measured emission levels include the type of nozzle and filter size-filter temperature interaction.

As described earlier, a separate laboratory study of temperature distributions and gradients in a Method 5 sampling train indicated that there can be substantial differences between external control temperature and gas temperature at the back of the probe. From this work, it is estimated that the actual gas temperature at the back of the probe for the Set 1 experiments was 150-160°C (300-320°F) rather than 120°C as inferred from the external reference temperature. As a result of this difference between Set 1 and Set 2 Method 5 experiments, several additional experiments were conducted on selected samples from the Set 2 grid. A comparison

TABLE 20

ANALYSIS OF VARIANCE TABLE FOR SET 2 EXPERIMENTAL GRID SAMPLES: FILTER CATCH PARTICULATE

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Value
Replicates	2	10.50	5.25	8.00
Blocks within reps	9	243.66	27.08	41.66
Filter Size	1	24.21	24.21	37.25
Temperature	1	0.69	0.69	1.06
Nozzle Type	1	7.42	7.42	11.42
Size Vs Temp Interaction	1	2.31	2.31	3.55
Size Vs Type Interaction	1	7.16	7.16	11.00
Temp Vs Type Interaction	1	0.12	0.12	0.18
Experimental Error	6	3.92	0.65	--

TABLE 21

SUMMARY OF THE ANALYSIS OF VARIANCE RESULTS
FOR THE SET # EXPERIMENTAL GRID SAMPLES

A. Summary of Data

	Probe	Filter	Total
Mean Particulate Catch (mg/m^3)	12.4	19.0	31.4
Standard Error (mg/m^3)	4.66	0.01	4.67
Coefficient of Variance (%)	38.0	4.2	15.0

B. Analysis of Variance Results

Significant Effects	Mean Difference (mg/m^3)	95% Confidence Internal (mg/m^3)
Probe catch	0	±4.6
Filter catch -		
• Filter Size:	2.5	1.7-3.3
• Nozzle Type:	1.4	0.6-2.2
• Size vs Type Interaction	1.3	0.5-2.1
Total catch -		
• Nozzle Type	5.8	2.2-11.4
• Size vs Temp Interaction	6.1	1.7-10.9

of sulfate contents in the probe and filter catches and a comparison to previous (Set 1) data on the basis of gas temperature at the back of the probe and filter temperature was given in Table 14. With respect to these data, there is little difference in sulfate content or distribution as a function of filter temperature. However, there is an indication of a higher level of sulfate collected in the probe for the higher probe gas temperature. Also the proportion of sulfate in the particulate is lower in the probe catch (and higher in the filter catch) for a gas temperature in the probe of 120°C. The significance of these observations is not considered very important due to the relatively small amounts of sulfate mass involved.

C. Additional Field Tests

Several additional field tests were conducted at the same oil-fired electric utility representing an extension of laboratory evaluations of in-stack particulate collectors. The sampling conditions and observed particulate distributions were presented earlier in Tables 15 and 16. Paired experiments were conducted in which one train (the B train) was run according to the Method 5 procedure and the A train either utilized an in-stack particulate collector or a quartz fiber external filter. The in-stack collector was the Svenska Flakt Jabriken (Sweden) thimble distributed in the United States by Carborundum Environmental Systems, Inc., Knoxville, Tenn. For our experiments, the thimble was slightly modified by increasing the pipe thread connections from 1/4 inch to 3/8 inch. The thimble was mounted in line with the probe axis, and was fitted with a buttonhook nozzle. The advantage of such a thimble over the flat filter arrangement utilized in Set 1 experiments is a substantially increased collection surface permitting more particulate to be collected with no significant increase in system pressure drop.

The experimental results for these comparative runs given in Table 16 indicates that the majority of the A train particulate is, in fact, collected in the thimble. An exception is noted for Run 3C in which more than half of the particulate was found in the nozzle; it is probable that the majority of this nozzle mass is extraneous, resulting from the nozzle scraping the side of the port during removal of the sampling train. Although some particulate is collected behind the thimble in these runs, the masses are relatively small and are not especially significant. Average distributions for the B train catch indicate about 40 percent in the probe and 60 percent on the filter. The comparative B/A ratios are not especially sensitive due to the very low levels of particulate mass collected.

These data are compared to the Set 1 experimental results in Figure 3, in which the Run 3B-APS sample was assigned a value of 2 mg/m3. The agreement between the sets of data is very good, providing additional support to the conclusions drawn from the Set 1 experiment grid samples.

Runs 37 and 38 were both carried out by the Method 5 procedure, with the A train utilizing a high purity quartz filter and the B train, a conventional MSA 1106 BH Filter. The quartz filter has the advantage of a very low chemical background (other than silica) and is therefore useful for in situ chemical analysis by such techniques as x-ray fluorescence analysis. The quartz filter was developed by Arthur D. Little, Inc., under EPA Contract No. 68-02-0585; the samples used here were from a pilot scale run carried out by Ralston, Ltd. Runs 37 and 38 yield almost identical results for the two trains, indicating an equivalence between the quartz and glass fiber filters for use in Method 5.

VI. CONCLUSIONS

Based upon the experimental studies described herein of particulate collection from an oil-fired steam boiler by Method 5 and in-stack collection procedures, the following conclusions are reached:

1. The Method 5 procedure does not lead to the formation of false particulate as a result of SO_2 oxidation or conversion to sulfate or by other mechanisms for the particular source conditions tested. Selective experiments involving enrichment in SO_2 by as much as an order of magnitude to levels of about 2000 ppm (representing combustion gases from fuel oil containing about 3% sulfur) likewise failed to indicate the formation of "false particulate" by Method 5 collection.

2. There is no evidence for chemical interactions involving transformations from the gas phase to particulate at any location within the sampling train that would have an influence on mass loading.

3. Based upon a set of experiments in which a research train with an in-stack collector was used as the control, selected variations to the Method 5 train resulted in no difference to the expected collection levels; variations included filter media (glass fiber vs quartz), filter temperature (120°C vs 150°C) and collection time (1 hr vs 2 hrs), where underlined conditions represent the Method 5 condition.

4. Based upon a straight line fit through the comparative Method 5 versus in-stack collector particulate loadings (normalized to 1 m^3), the Method 5 train was observed to collect about 20 percent less particulate than the in-stack procedure. Also, a blank correction of 10-15 mg/m^3 was indicated for the Method 5 train. It is thought that these differences are due to the difficulties of obtaining a quantitative recovery of the probe catch.

5. Particulate collected by the Method 5 train typically contained 40 percent sulfate, irrespective of filter temperature for the range 120-150°C. With a gas temperature at the back of the probe of approximately 150°C, both filter and probe catches contained ~40 percent sulfate, but for a temperature of 120°C, the distribution of sulfate was ~17 percent in the probe catch and ~57 percent in the filter catch. The total particulate distributions between the probe and filter were about equal at the higher gas temperature as compared to a 37-63 percent distribution, respectively, for the lower gas temperature. In summary, less of the particulate (and sulfate) is caught in the probe for a gas temperature of 120°C

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compared to approximately equal probe-filter catches for a gas temperature of ~150°C. Because of the substantially lower standard error for the filter catch compared to the probe catch (i.e., ~1 mg/m³ versus ~5 mg/m³, respectively, as given in Table 21), there is an advantage in maintaining the gas temperature at the back of the probe at ~120°C.

6. The type of nozzle (buttonhook versus 90 degree bend) and a combined filter size-temperature interaction (8.3 cm versus 10 cm dia and 120°C versus 150°C) are found to have a statistically significant result on the level of the particulate catch, with differences of 6 to 7 mg/m³ with an experimental uncertainty of ±5 mg/m³.

7. For Method 5 testing, the probe catch exhibits a standard error of 5 mg/m³ and a coefficient of variation of 40 percent, compared to 1 mg/m³ and 5 percent, respectively, for the filter catch.

The above conclusions are made with respect to the particular stationary source studied and are not necessarily valid for all oil-fired steam generators. For example, combustion of a high sulfur fuel could yield stack gases with a SO_3 content of 5 ppm or higher. If the probe and filter temperatures were maintained at 150°C, the SO_3 would remain in the vapor state, and none should be collected. At 120°C, however, amounts corresponding to 10 mg/m³ or more would be collected as particulate. Such a situation could alter some of the conclusions, such as No. 5 given above.

In terms of these observations, there appears to be an advantage in utilizing an in-stack train for particulate sampling. In this way, sample recovery from the probe is precluded, thus, eliminating the largest source of error in the Method 5 procedure. Also, any condensation of SO_3 in the probe or on the external filter would not be included in the particulate catch. Finally, the design,operation and sample recovery aspects of an in-stack particulate train could be greatly simplified with respect to the present Method 5 procedure.